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Design of a Plant for the Production of Ammonia and Urea Using Aspen Hysys

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ABSTRACT

The Design of a Plant for the production of 1800MT/Day of Ammonia and 1400MT/Day of Urea using aspen hysys was carried out in this work. Ammonia is produced through the Haber-Bosch process, where hydrogen and nitrogen react in the presence of a catalyst producing mixture containing ammonia while urea is produced by the reaction between ammonia and carbon IV oxide. In this work, Aspen HYSYS, chemical Engineering design software was used to design and perform material and energy balance around the plant. From the design analysis performed from the software, plant production capacity of 75,063kg/hr of ammonia and 58,343kg/hr of Urea was obtained. 7,677.6kmole/hr of methane gas, 19,194kmol/hr of steam and 3,584kmol/hr of air feeds was used to achieve the objective. The overall reaction is exothermic and the primary reformer process is characterized by a low pressure. Cost estimation carried out showed that the total purchased cost of equipment was $9,881,055 fixed capital investment was $64,545,522, gross annual earning was $72,422,247, and net annual income was $54,316,685 rate of return was 38.85% and payback time was 2.5years. Safety consideration for a smooth run of the ammonia-urea plant is also presented in this work.

Keywords: Design, Plant, production, ammonia, Urea, Aspen Hysys

INTRODUCTION

The production of ammonia and urea has been researched by various researchers as well as the basic raw materials was identified and grouped as an agricultural product [1]. Agriculture dominates the world market; ammonia is mainly used to produce urea. Urea is a phytonutrient used to grow crops. The urea (fertilizer) market is expected to expand. According to the 2018-2022 fertilizer outlooks, with the increase of the world's population, especially the population of Nigeria, the demand for fertilizers in the global market has grown moderately, resulting in insufficient supply of fertilizer (urea). In addition to agriculture, the demand for ammonia in pharmaceutical, pulp and paper, food, and petroleum industries is also increasing. as more and more industries need this product [2]. There is an urgent need to build more ammonia and urea production plants to curb shortages and inefficient supply of fertilizers (urea). The article is aims to design a processing plant to provide higher production of the required products with lower energy consumption [3-5]

Researchers work conducted on ammonia revealed that ammonia is an essential raw material use by various industries as well as one of the major raw materials used in the production of 'urea.

Ammonia is produced commercially by the reaction between hydrogen gas (H_2) and nitrogen gas (N_2), while urea (NH_2CONH_2) is synthesized from the reaction between ammonia and carbon dioxide [6]. Ammonia is use to make fertilizers, Refrigerant, Explosives, Dyes, House hold cleaners. Urea is used as a fertilizer, to grow food, Used in Plywood (Urea formaldehyde), Explosives (Urea-nitrate) etc

Investigation carried out revealed that urea plays an important role in the metabolism of nitrogen-containing compounds in animals and is the main nitrogen-containing substance in mammalian urine. It is a colorless, odorless solid, highly soluble in water and virtually non-toxic, neither acid nor alkaline. The body uses it in many processes, the most notable being the excretion of nitrogen [7-8].

Research was conducted in the production of ammonia ammonia in 1754 by heating the "subamoniac (ammonium chloride) with lime. The new compound was called to cut the arm of the Egyptian god, because ammonium chloride was first produced in the 4th century BC. of camel dung near the temple of the severed arm [9].

The hydrogen for the ammonia synthesis was made by water gas process (a Carl–Bosch process) which involves blowing steam through a bed of red hot coke resulting in the separation of hydrogen by distillation of liquid air, then by cooling and compressing air [10].

Nowadays, the hydrogen is produced by reforming light petroleum fractions or natural gas (methane CH4) by adding steam. The most used process in ammonia-urea production is the Haber - Bosch process [11-14].

Design method

The design was carried out using Aspen Hysys (V11) and the steps are as follows:

I. Choose component

Components such as CH_4, CO_2, CO, H_2O, NH_3, N_2, H_2, air, NH_2CONH_2, and saved it as component list one.

II. Select fluid package (Peng-Robinson preferable)

Pen-Robinson was chosen because it is the most compatible fluid package for Vapor -Liquid equilibrium calculations, and it covers wide range of operating condition.

III. Add all the reaction set which include; -Reformer Reaction, -Shift conversion Reaction, Methanation Reaction , -Ammonia Synthesis reaction and Urea Synthesis Reaction

Reformer reaction was modeled as Equilibrium and Conversion Reaction since the data for rate constant (K) and Temperature are available in the software

The Haber process (Ammonia synthesis) was modeled as a simple rate reaction by using a plug flow reactor, the constant in the Arrhenius equation was obtain from the literature, Reaction set were defined and after which the design is ready

The PFD were constructed from the simulation basis environment, run, and all data calculated. It was then optimized to give the required output and various results printed. The hysys flow diagram of the design is presented in figure 1 shown below

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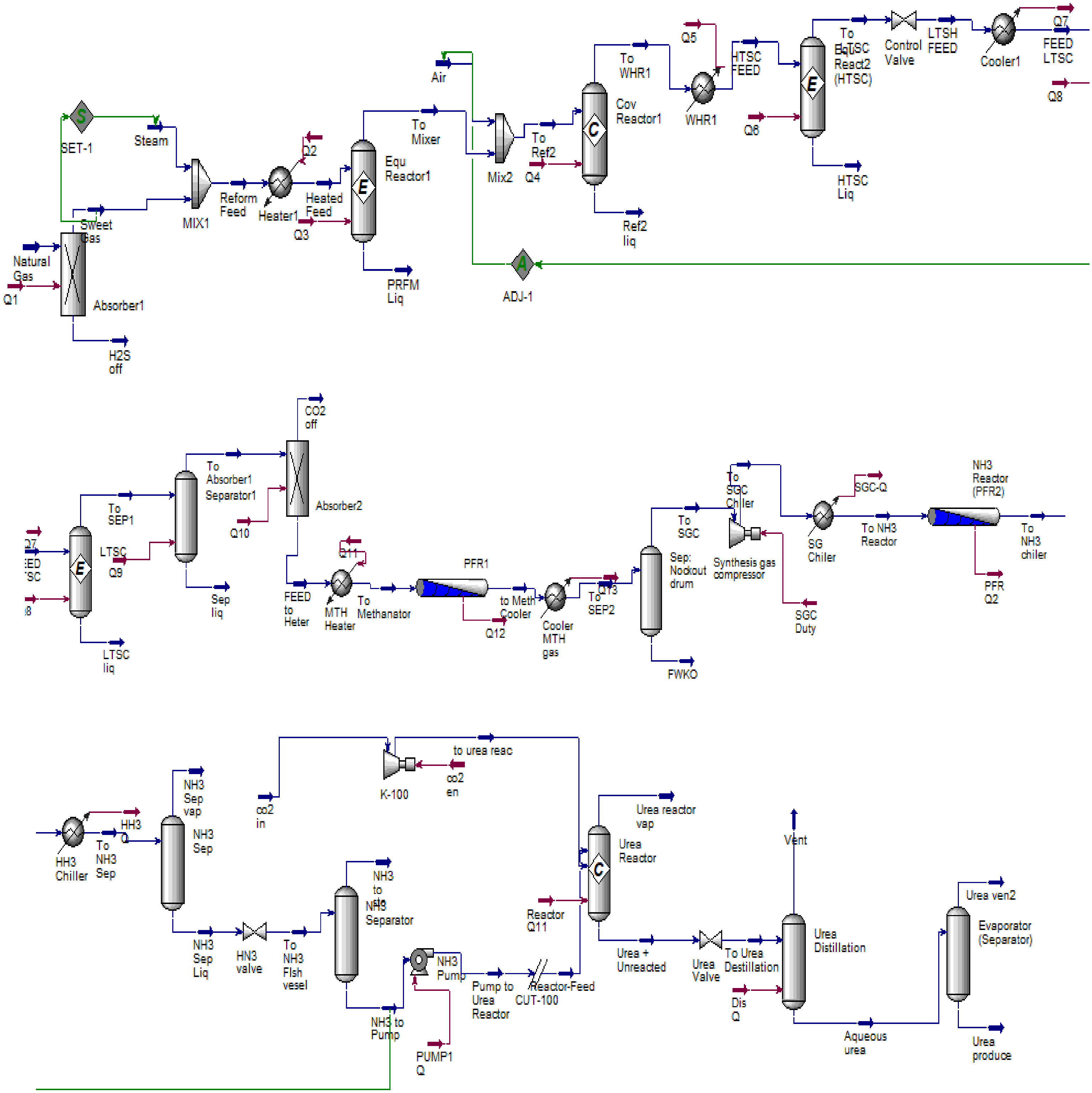

Figure 1: Simulated Process Flow Diagram

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General Material Balance Equation

$$\begin{pmatrix}\text{Rate of accumulation}\\ \text{of Production}\\ \text{within the reactor}\\ \text{volume per time}\end{pmatrix} = \begin{pmatrix}\text{Rate of input}\\ \text{of Feed (i) into the}\\ \text{reactor volume per}\\ \text{time}\\ .\end{pmatrix} - \begin{pmatrix}\text{Rate of output}\\ \text{of materials out}\\ \text{of the reactor}\\ \text{volume per time}\end{pmatrix} + \begin{pmatrix}\text{Rate of depletion}\\ \text{of materials due to}\\ \text{chemical reactions}\\ \text{in the ractor volume}\\ \text{per time}\end{pmatrix} \quad (1)$$

For the design of the ammonia urea plant, the following assumptions were made
The plant operates in a continuous manner
The process is a steady state operation
All gases are assumed to be ideal and conform to the ideal gas equation

Design basis
Time basis: 1hour
Estimated output for ammonia: 1800MT/day
Estimated output for urea: 1400MT/day

Material Balance over the Plug Flow Reactors

The material balance of the plug flow reactor used for the research work is illustrated in figure 2

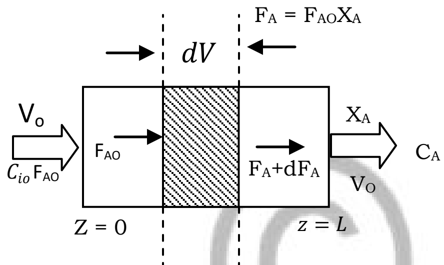

Figure 2: Notation for plug flow reactor

The various terms in equation (1) are obtained mathematically as follows:
(Rate of accumulation of component i) = 0 (2)
(Rate of input of component i) = F_{AO} (3)
(Rate of output of component i) = $F_A + dF_A$ (4)
(Rate of depletion of component i) = $(-r_i)dV$ (5)
Substituting terms into eq. (1) gives:
$0 = F_A - (F_A + dF_A) + (-r_i)dV$
Hence $dF_A = (-r_i)dV$ (6)
Recall that $F_A = F_{AO}X_A$, substitute into equation 6, we obtain
$d(F_{AO}X_A) = (-r_i)dV$ (7)

$$\int_0^{VR} dV = F_{AO}\int_0^{XA} \frac{dXA}{(-r_i)}$$

$$V_R = \frac{FAoX\,A}{(-r_i)} \quad (8)$$

Length of PFR

Recall: Volume of Cylinder is given as:

$$V = \frac{\pi D^2 H}{4} \quad (9)$$

Making Length (L_R) the subject of formula

$$L_R = \frac{4V_R}{\pi D^2} \quad (10)$$

Kinetics Analysis

Consider ammonia synthesis reaction below
The reaction is between nitrogen and hydrogen to produce ammonia.

$$N_2 + 3H_2 \underset{K_2}{\overset{K_1}{\Leftrightarrow}} 2NH_3$$

$A + 3B \rightarrow 2C$

Let A = N_2, B=H_2, C=NH_3

Applying the principle of rate law which states that, the rate of reaction is directly proportional to the concentration of the reactants we have the rate of the reaction for ammonia synthesis as:

$$r_i = k_1 C_A \left(\frac{(C_B)^3}{(C_C)^2}\right)^{\alpha} - k_2 \left(\frac{(C_C)^2}{(C_B)^3}\right)^{1-\alpha} \quad (11)$$

Where;

α = Temkin parameter (0.4-0.5)

Where: K_1 is the rate constant given by Arrhenius equation as:

$$K_1 = A_0 \exp\left(-E_A/_{RT}\right) \quad (12)$$

RESULTS AND DISCUSSION

Converting the Production Capacity from $\frac{Mtons}{day}$ to $\frac{kg}{h}$

Taking 330days as operational days out of the 365days in a year.

For Ammonia

$$18000\frac{Mtons}{day} * \frac{1000\,kg}{1Mton} * \frac{1day}{24hr} = 75000\frac{kg}{hr}$$

For Urea

$$14000\frac{Mtons}{day} * \frac{1000\,kg}{1Mton} * \frac{1day}{24hr} = 58333.33\frac{kg}{hr}$$

Summary of Material Balance results around each Process Equipment (all data calculated by Hysys)

The summery of the material balance in terms of the results obtained from each process equipment is presented figure 3 for steam reformer mixer and the input and output data for components of H_2O ad CH_4 is shown in Table 1

Steam Reformer mixer

System: Mixer

Balance: steady state

Time basis: 1hour

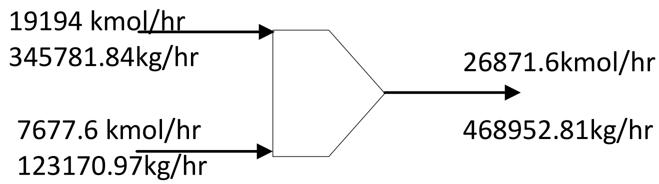

Figure 3: Steam Reformer Mixer

Table 1: Material Balance on Mixer

Components	Input		Output	
	Mole	Mass	Mole	Mass
H_2O	19194	345781.84	19194	345781.84
CH_4	7677.6	123170.97	7677.6	10987.68

Total	26871.6	468952.81	26871.6	468952.81

Primary Reformer

The material balance of primary reformer is demonstrated in figure 4 in terms of input and output as well as mole and mass value of components is presented I Table 2

System: Primary reformer (reactor)

Balance: steady state

Time basis: 1hour

Chemical Reaction: $CH_4 + H_2O \rightarrow CO + 3H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

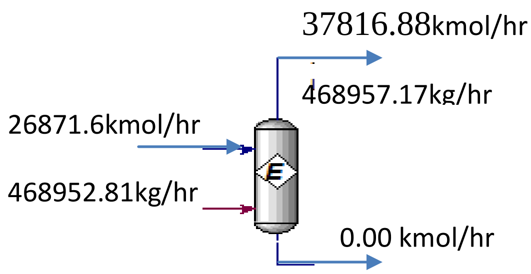

Fig 4: Primary Reformer

Table 2: Material balance on Primary Reformer

Components	Input		Output	
	Mole	Mass	Mole	Mass
CH_4	7677.60	345781.84	2204.96	35374.03
H_2			18526.54	37349.50
H_2O	19194.00	123170.97	11612.74	209204.68
CO_2			2108.62	92799.80
CO			3364.02	94229.15
Total	26871.6	468952.81	37816.88	468957.17

Air Reforming Mixer

The air reformer mixer of the input and output material balance is shown in figure 5 as well as the components mile and mass value, is shown on Table 3

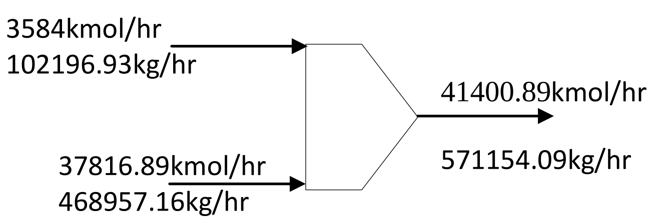

Fig 5: Air Reformer mixer

Table 3: Material balance on air Reformer mixer

Components	Input		Output	
	Mole	Mass	Mole	Mass

CH_4	2204.96	35374.03	2204.96	35374.03
H_2	18526.54	37349.50	18526.54	37349.50
H_2O	11612.74	209204.68	11612.74	209204.68
CO_2	2108.62	92799.80	2108.62	92799.80
CO	3364.02	94229.15	3364.02	94229.15
N_2	3347.53	93774.48	3347.53	93774.48
Ar	107.63	4299.70	107.63	4299.70
O_2	128.84	4122.75	128.84	4122.75
Total	41400.89	571154.09	41400.89	571154.09

CO_2 Absorber

Figure 6 demonstrates the CO2 absorber input and output values and the material balance of CO_2 absorber in terms of input and output values of the mole and mass is shown in Table 4

System: Absorber
Balance: steady state
Time basis: 1hour

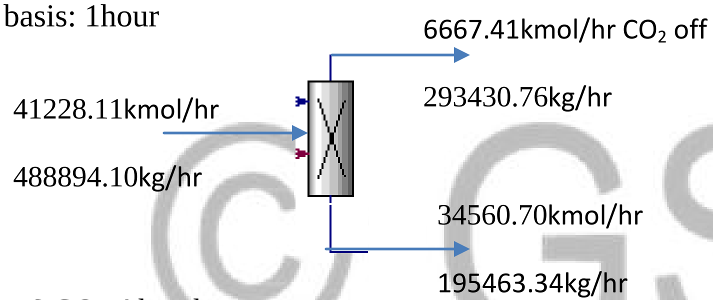

Figure: 6 CO_2 Absorber

Table 4: Material balance on CO_2 Absorber

Components	**Input**		**Output**	
	Mole	Mass	Mole	Mass
CH_4	5.51	88.44	5.51	88.44
H_2	29581.10	59635.50	29581.10	59635.50
H_2O	497.06	8954.59	497.06	8954.59
CO_2	6667.41	293430.76	6667.41	293430.76
CO	1000.01	28011.08	1000.01	28011.08
N_2	3347.44	93771.91	3347.44	93771.91
Ar	107.63	4299.69	107.63	4299.69
O_2	21.94	702.13	21.94	702.13
Total	41228.11	488894.10	41228.11	488894.10

Ammonia Sythesis Converter

Figure 7 Illustrates the input and output values of ammonia synthesis converter and the material balance values of components of input and output is shown in Table 5
System: Ammonia synthesis converter (reactor)
Balance: steady state
Time basis: 1hour

Chemical Reaction: $N_2 + 3H_2 \Leftrightarrow 2NH$

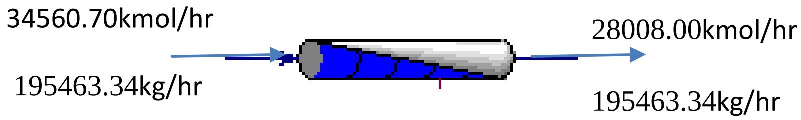

Figure 7: Ammonia Reactor (Plug flow)

Table 5: Material balance on NH_3 Reactor (plug flow reactor)

Components	Input		Output	
	Mole	Mass	Mole	Mass
CH_4	5.51	88.44	5.51	88.44
H_2	29581.10	59635.50	19752.06	39820.15
H_2O	497.06	8954.59	497.06	8954.59
CO	1000.01	28011.08	1000.00	28011.08
N_2	3347.44	93771.91	71.094	1991.55
Ar	107.63	4299.69	107.63	4299.69
O_2	21.94	702.13	21.94	702.134
NH_3	0.00	0.00	6552.70	111592.45
Total	34560.70	195463.34	28008.00	195463.34

System: **Ammonia Separator**

Figure 8 demonstrates the input and output values of the separator whereas the components values of the input and output is presented in Table 6

Balance: steady state
Time basis: 1hour

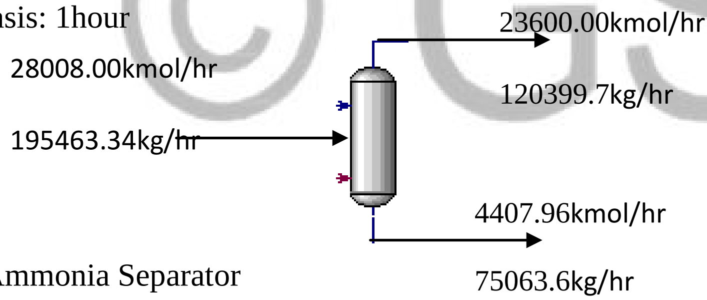

Fig 8: Ammonia Separator

Table 6: Material balance on Ammonia Separator

Components	Input		Output	
	Mole	Mass	Mole	Mass
CH_4	5.51	88.44	5.51	88.44
H_2	19752.06	39820.15	19752.06	39820.15

H_2O	497.06	8954.59	497.06	8954.59
CO	1000.00	28011.08	1000.00	28011.08
N_2	71.094	1991.55	71.094	1991.55
Ar	107.63	4299.69	107.63	4299.69
O_2	21.94	702.134	21.94	702.134
NH_3	6552.70	111592.45	6552.70	111592.45
Total	28008.00	195463.34	28008.00	195463.34

Flash Vessel

System: Flash vessel (separator)
Balance: steady state
Time basis: 1hour

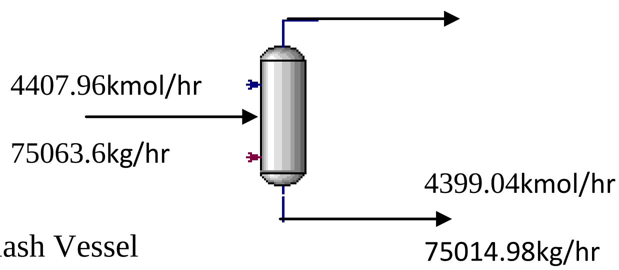

Fig 9 Flash Vessel

Figure 9: showcases the flash vessel input and output value whereas Table 7 demonstrates material balance of flash vessel in terms of components of input and output values.

Table 7; Material balance on Flash Vessel

Components	**Input**		**Output**	
	Mole	Mass	Mole	Mass
CH_4	0.037	0.59	0.037	0.59
H_2	36.83	74.26	36.83	74.26
H_2O	496.40	8942.64	496.40	8942.64
CO	1.19	47.45	1.19	47.45
N_2	0.11	3.12	0.11	3.12
Ar	2.64	73.89	2.64	73.89
O_2	0.18	5.79	0.18	5.79
NH_3	3870.58	65915.91	3870.58	65915.91
Total	4407.96	75063.66	4407.96	75063.66

Urea Synthesis Tower

Figure 10 demonstrates the urea synthesis tower input and output values whereas the material balance of urea reactor is shown in Table 8.

System: Urea synthesis tower (reactor)
Balance: steady state
Time basis: 1hour
Chemical Reaction: $2NH_3 + CO_2 \Leftrightarrow NH_2COONH_4$

$$NH_2COONH_4 \Leftrightarrow CO(NH_2)_2 + H_2O$$

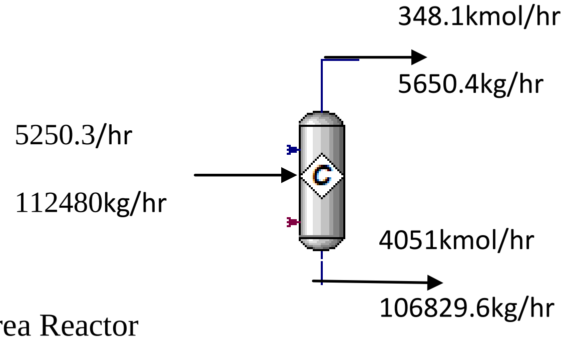

Fig 10: Urea Reactor

Table 8: Material balance on urea Reactor

Components	Input		Output	
	Mole	Mass	Mole	Mass
CH_4	0.0344	0.55	0.0344	0.55
H_2	29.57	59.62	29.57	59.62
H_2O	496.40	8942.64	1527.79	27523.16
CO	1.14	45.60	1.14	45.60
N_2	0.087	2.43	0.087	0.087
Ar	2.25	63.09	2.25	63.09
O_2	0.17	5.49	0.17	5.49
NH_3	3869.38	65895.56	1403.91	26448.403
CO2	851.3	37464.00	0.00	0.00
Urea	0.00	0.00	1254	58334.0
Total	5250.3	112480	5250.3	112480

Urea Separator

Figure 11: illustrates the urea separator input and output values whereas the material balance of urea separator is shown in Table 9 for the different input and output components.

System: Flash vessel 2 (separator)
Balance: steady state
Time basis: 1hour

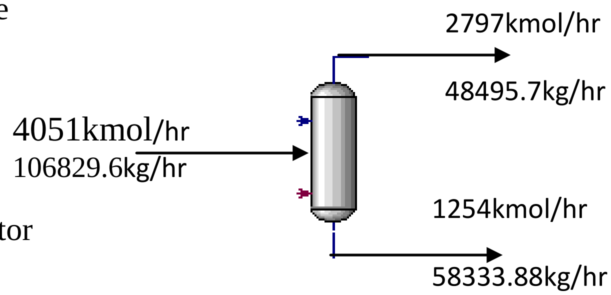

Fig 11: Urea Separator

Table 9: Material Balance on Urea Separator

Components	Input		Output	
	Mole	Mass	Mole	Mass
H_2	10.008	20.18	10.008	20.18

H_2O	1727.99	22027.42	1727.99	22027.42
NH_3	1059	26448	1059	26448
Urea	1254	58334	1254	58334
Total	4051	106829.6	4051	106829.6

Urea Evaporator

Figure 12 demonstrates the input and output values of the evaporation units whereas the table 10 showcases the input and output values of the urea in terms of mole and mass

System: Evaporator (separator)
Balance: steady state
Time basis: 1hour

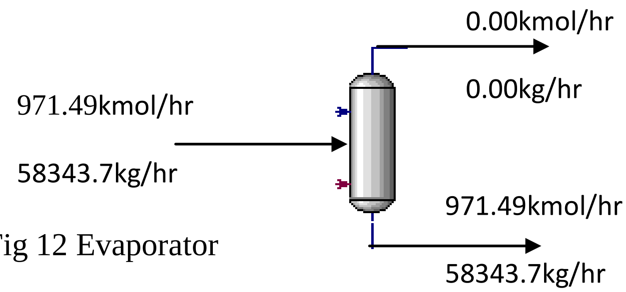

Fig 12 Evaporator

Table 10: Material balance on Evaporator

Components	Input		Output	
	Mole	Mass	Mole	Mass
Urea	971.49	58343.7	971.49	58343.7
Total	971.49	58343.7	971.49	58343.7

Summary of Equipment Design

Table 11 to 16 illustrates the properties of the design parameters for primary reformer, secondary reformer, methanator unit, ammonia synthesis converter unit, urea synthesis converter unit, ammonia Separator and urea separator and the parameters considered include temperature, pressure, conversion, feed rate, configurations, orientation, percentage loading, height, diameter, volume, thickness of shell, material of construction, allowable stress etc as detail required parameters are well reported in each sub heading in this research work.

Primary Reformer

Equipment type: reactor
Category: fixed bed reactor
Balance: steady state
Time basis: 1hour

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

Percentage conversion: 30%

Table 11: Design for Steam reformer reactor

Design parameters	Description
Temperature	550^0C

Pressure	490kpa
Conversion	30%
Feed rate	468952.81 kg/hr
Configuration	Cylindrical column with hemispherical ends
Orientation	Vertical
Height	5.585m
Diameter	3.725m
Volume	61m^3
Thickness of shell	0.0085m
Material of construction	304 stainless steel
Allowable stress	1.18*10^{8}N/m^2

Secondary Reformer
Equipment type: reactor
Category: fixed bed reactor
Balance: steady state
Time basis: 1hour
Chemical Reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Table 12: Design for Air Reform Reactor

Design parameters	**Description**
Temperature	1000^{0}C
Pressure	480kpa
Conversion	44%
Feed rate	571154.099kg/hr
Configuration	Cylindrical column with hemispherical ends
Orientation	Vertical
Height	6.70
Diameter	4.467m
Volume	105m^3
Thickness of shell	0.010m
Material of construction	304 stainless steel
Allowable stress	1.18*10^{8}N/m^2

Methanator
Equipment type: reactor
Category: fixed bed reactor
Balance: steady state
Time basis: 1hour
Chemical Reaction: $CO + 3H_2 \rightarrow CH_4 + H_2O$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Ammonia Synthesis Converter
Equipment type: reactor
Category: plug flow reactor
Balance: steady state
Time basis: 1hour
Chemical Reaction: $N_2 + 3H_2 \Leftrightarrow 2NH_3$

Table 13: Design for Ammonia Reactor

Design parameters	Description
Temperature	250^0C
Pressure	13725.0kpa
Conversion	95%
Feed rate	195500 kg/hr
Configuration	Cylindrical column with hemispherical ends
Orientation	Horizontal
Length	6.2m
Diameter	3.6m
Volume	$21m^3$
Thickness of shell	0.24m
Material of construction	304 stainless steel
Allowable stress	$1.18*10^8 N/m^2$

Urea Synthesis Tower

Equipment type: reactor
Category: fixed bed reactor
Time basis: 1hour
Chemical Reaction: $2NH_3 + CO_2 \Leftrightarrow NH_2COONH_4$
$NH2COONH4 \Leftrightarrow CO\ (NH2)2 + H2O$

Table 14: Design for Urea Reactor

Design parameters	Description
Temperature	30.93^0C
Pressure	12000.00kpa
Conversion	96%
Feed rate	75014.976 kg/hr
Configuration	Cylindrical column with hemispherical ends
Orientation	Vertical
Height	6.1m
Diameter	4.075m
Volume	$79.7m^3$
Thickness of shell	0.24m
Material of construction	304 stainless steel
Allowable stress	$1.18*10^8 N/m^2$

Ammonia Separator

Equipment type: Absorber
Balance: steady state
Time basis: 1hour

Table 15: Design for NH_3 Separator

Design parameters	Description
Temperature	30^0C
Pressure	13675.0kpa
Area	$9.073m^2$
Configuration	Cylindrical column with hemispherical ends

Orientation	Vertical
% loading	60%
Height	8m
Diameter	4m
Volume	100.5m^3

Urea Separator
Equipment type: Absorber
Balance: steady state
Time basis: 1hour
Table 16: Design for Urea Separator

Design parameters	Description
Temperature	183^{0}C
Pressure	12000kpa
Area	9.073m^2
Configuration	Cylindrical column with hemispherical ends
Orientation	Vertical
% loading	60%
Height	8m
Diameter	4m
Volume	103.6m^3

3.3 Discussion of Results

From the feed stock; methane, steam and air with the flow rate of 7678kmol/hr CH_4, 19190kmol/hr steam, and 3584kmol/hr air. The targeted plant production capacity of 4407.94kmol/hr (75063.6kg/hr) of ammonia and 971.49kmol/hr (58334kg/hr) of urea was obtained. In the steam methane reforming, 29581.10kmol/hr of hydrogen was produced which combined with 3347.44kmol/hr Nitrogen in the ammonia synthesis reactor.

Material and energy balance results for each of the equipment as well as equipment design has been provided in chapter 3, the equipment design performed shows that the volume of ammonia reactor is 21m^3, length 6m, diameter 3m, and shall thickness 0.27m. The volume of urea reactor is 79.7m^3, height 6.1m, diameter 4.075m, and thickness of shall 0.24. Volume of ammonia separator is 100.5m^3, that of urea is 103.6m^3 and Absorber (component splitter) is 196.35m^3.

The ammonia-stripping urea process involves high ammonia to carbon iv oxide ratio in the reactor ensuring high conversion of carbamate to urea. The technology used in this research work differs from other competitors because of the ease of modification, energy efficient, low operating cost and high conversion of carbamat to urea and the use of excess ammonia to avoid corrosion as well as to promote the decomposition of unconverted carbamate into urea.

Cost estimation carried out show that the total purchased cost of equipment is $9,881,055, fixed capital investment is $64,545,522, gross annual earning is $72,422,247, Net annual income is $54,316,685, Rate of return is 38.85% and payback time is 2.5years. The payback time falls within the range of payback period which is between 2–5 years for a typical chemical Engineering plants [15]. This suggests that at this point in time of the project life, the gross profit generated up to this point would be enough to pay off the initial capital investment.

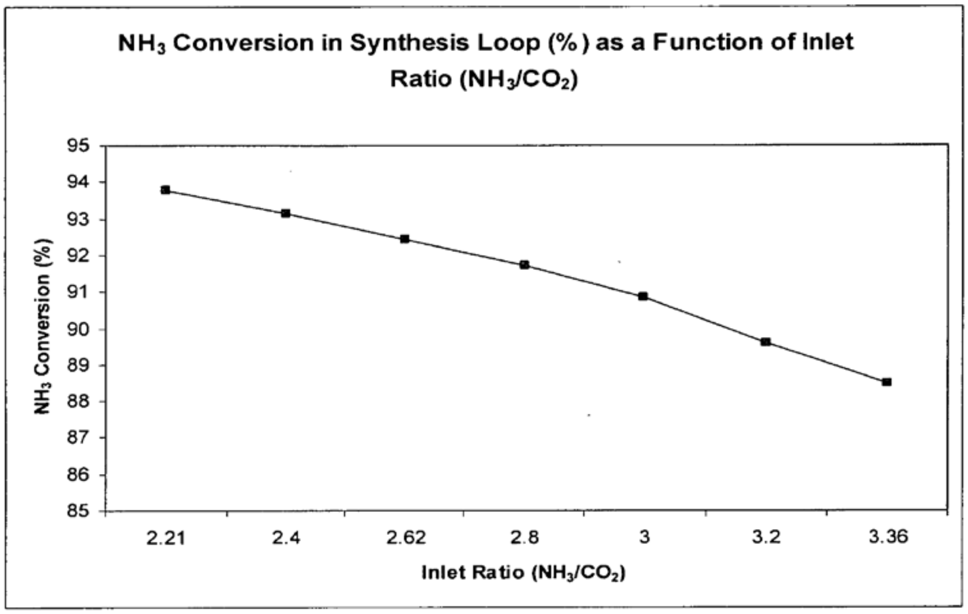

Figure 13: Effect of temperature and pressure on % conversion

From the graph above, a low temperature and higher pressure increases the % conversion of the feed gas to ammonia, but in order to achieve the objective, the temperature have to set to 756^0C and pressure of 13765kpa which are the values obtained from the literature as well as in figure 13

(b) Effect of Catalyst

Catalyst speed up the rate of chemical reaction either by allowing different reaction mechanism or by providing addition mechanism, the overall effect is to lower activation energy (i.e it provide an alternative pathway with lower activation energy), it increases the reaction rate

General Analysis

After building the flow-sheet in the simulation environment, try by error method was used to optimize the plant in order to achieve my targeted plant capacity.

Try by error method was also used in the heat integration network to improve the efficiency of the plant and to save cost and have good economic performance

Figure 14: NH_3 conversion to Urea in synthesis loop as a function of inlet ratio

Figure 14 shows the relationship between conversions of ammonia to urea in the synthesis loop with the inlet ratio NH_3/CO_2. As the inlet ratio is decreased, the overall loop conversion of NH_3 to urea is increasing

CONCLUSION

The simulation of Ammonia-Urea process carried out in this work using Aspen Hysys yield accurate results and the targeted plant capacity was achieved with ease of modification. The Sizing of all the units and results produced throughout the research work has been presented. The process is more environmentally responsible than other ammonia-urea process routes. The product quality depends on the maintenance of appropriate temperature & pressure conditions in the reactors. Moreover, to enhance ammonia-urea production, a recycle stream was installed for more production

Contribution to Knowledge

The Contribution of this research work in line with the objectives is as follows;

Design of an integrated process for the production of ammonia and urea using aspen hysys. A combined ammonia and urea process plant with the giving plant capacity was achieved in this design work, this is the first of its kind

Plant is free from carbon emission. The plant reduces environmental hazards that could result from the effluent by installing a recycle unit, these effluents are treated in the plant and returned in the reactor for further production

Optimization of the developed process in aspen hysys

The hysys model developed can be easily modified

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